The Nature of the HB. 1. HB Empirical Rules from Crystal Structure Correlations

Gastone Gilli, Valeria Ferretti, Valerio Bertolasi, Paola Gilli
Chemistry Department and Centre for Structural Diffractometry, University of Ferrara, Ferrara, Italy. E-mail: ggilli.chim@unife.it

HB is a D•–•H---:A three-centre-four-electron proton-shared interaction characterized by an extreme variability of HB properties (energy, geometry, shape of the proton-transfer pathway, electrostatic/ covalent nature) even for a same D…A couple of donor and acceptor atoms. Not surprisingly, its complete rationalization has turned out to be a formidable problem. This communication shows that the partial results obtained by systematic CSD screening over the years can now be unified to give a coherent interpretation of all factors determining HB strength in any molecular system. It is shown that all HBs can be reduced to only six specific molecular patterns, the six Chemical Leitmotifs (CL), out of which *four* have the curious property of turning *weak, long and proton-out-centred HBs of electrostatic nature* into *strong, short and proton-centred ones classifiable as 3-center-4-electron covalent bonds*, and *the last two* are deputed to form the moderately strong σ-cooperative …O-H…O-H…O-H… bonds typical of water or the almost infinite variety of weak HBs.

CLs are interpreted in terms of differences of proton affinities (PA) or acid-base dissociation constants (pK_a) of the HB donor and acceptor group, showing that all HB phenomenology can be reduced to a more basic "PA/pK_a Equalization Principle" stating that the HB properties are completely determined by the differences of these quantities (PA or pK_a) and that the strongest possible HB can only be associated with the conditions ΔPA or $\Delta pK_a = 0$.

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